6 Summary

In this work a new machine for the examination of ion-molecule-reactions was planned and built. The focus was the analysis of reaction constants and correspondingly cross sections at low c.m.-energies. To achieve this goal it was necessary to connect an ion-guide with a quadrupole mass spectrometer, where the ion-guide was operated in energy-conserving (adiabatic) mode. The four poles of the ion-guide, a quadrupole itself, were constructed with 15 wires each, arranged in a hyperbolic form (Chapter 3.2). This design has some major advantages compared to quadrupoles with solid poles:

- The hyperbolic form of the electrodes is easier to construct with wires than with solid metal.
- Bigger electrodes and therefore greater distances between the electrodes are easier to build.
- Greater distances between electrodes also result in greater distances between ions and electrode surfaces; thereby minimizing field disturbances caused by e.g. corroded electrodes or not optimally mounted wires.
- The open design makes it easier to evacuate the reaction chamber.
- Due to the modular concept of the design it is possible to build various multipoles on a low time and cost basis.

The core piece of the ion-guide is the rf-generator (Chapter 3.3). It was constructed by an efficient design using two radio tubes. Frequency and amplitude were adjusted according to the needs of the experiment. Compared to semiconductors, tubes have some major advantages. On one hand they are more powerful and short-circuit-proof and on the other hand they are much cheaper. Furthermore, a rf-generator with radio tubes can be built with much less components than one with semiconductors; this considerably simplifies the tuning process and troubleshooting.

The analysis of the effective c.m.-energy was more difficult than originally assumed. Multiple effects can influence the c.m.-energy: besides the acceleration energy of the ions, there is (i) the radial energy by the rf-field and (ii) the Doppler broadening because of the Maxwellian velocity distribution of the target molecules (Chapter 4.3.2). The amount of radial energy considerably depends on the point of ionisation (Fig. 4-8) and has to be redetermined with each change in the experimental setup. Since a direct measurement of the radial energy is not possible one has to rely on calculations with SIMION 3D (Fig. 4-10). The Doppler broadening always occurs when the target molecules have a Maxwellian velocity distribution, which depends on the temperature and can be calculated as follows,

Eq. 2-37 $$W_{½} = (11.1 \gamma k T E_0)^{½}.$$

Both the Doppler broadening effect, as well as the radial energy influence have been incorporated in the calculation of errors for the c.m.-energy (Chapter 4.3.2).

The second part of the present study involves the investigation of four ion-molecule reactions. With the help of these reactions (i) the functional efficiency of the machine could be proofed and (ii) initial measurements of k-values at low c.m.-energies (< 1 eV) were made. The following ion-molecule reactions were investigated:

4.1 $HBr^+ + HBr \rightarrow H_2Br^+ + Br\cdot$ (ΔH = -0.35 eV)

4.2 $HBr^+ + CO \rightarrow HCO^+ + Br\cdot$ (ΔH = -0.43 eV)

4.3 $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ (ΔH = -0.57 eV)

4.4 $NH_3^+ + H_2CO \rightarrow CH_2NH^+ + H_2O$ (ΔH = -0.21 eV)

The first reaction, $HBr^+ + HBr \rightarrow H_2Br^+ + Br\cdot$, was used to determine an accurate k-value at a defined c.m.-energy, and ultimately to verify the functional efficiency of the assembly. The results of this experiment are summarised in Tab. 6-1. The k-value calculated from this work is in agreement

with the theory and k-value given by Zare and co-workers. In addition the error margin could be reduced by approximately 10% (Chapter 4.1).

The second reaction, $HBr^+ + CO \rightarrow HCO^+ + Br\cdot$, could be also investigated. However, both this and the first reaction had to be discontinued since HBr corroded the turbo molecular pumps, which subsequently resulted in their breakdown. For this reason the less corrosive system with ammonia was selected.

method	**k-value** $\cdot 10^{-10}$ **cm^{3}s^{-1}**	**cross section** $\cdot 10^{-19}$ **m^2**
this work	(5.6 ± 0.83)	(1.27 ± 0.19)
Langevin	7.56	1.71
Locked Dipole	8.51	1.93
Zare[63]	(6.7 ± 1.6)	(1.52 ± 0.37)

Tab. 6-1: comparison of experimental data from HBr^+ + HBr with theoretical calculations and literature value at c.m.-energy of 3.5 eV (except Zare)

The third reaction, $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$, was utilised to measure the first k-values at c.m.-energies from 0.06 eV to 3.5 eV. The results are summarised in Abb. 6-1 (comp. Fig. 4-14). The exponential fit of the experimental data correlates well with Langevin (Eq. 4-4) and Locked Dipole (Eq. 4-5) theoretical calculations. At c.m.-energies lower than 0.5 eV, a greater spreading of the k-values was observed. To overcome this problem in future investigations, the c.m.-energy control should be improved by using the molecular beam technique and better-stabilized power supplies for polebias, acceleration lenses and rf-amplitude.

The fourth reaction, $NH_3^+ + H_2CO \rightarrow CH_2NH^+ + H_2O$, was not observed, even though the reaction is exothermic at -0.21 eV. According to calculations from Walch[108], this reaction has a non-negligible second reaction barrier of

approximately 35kcal/mol = 1.513 eV. This implies that the reaction conditions originally planned were not suitable to form CH_2NH^+ in quantities large enough to detect.

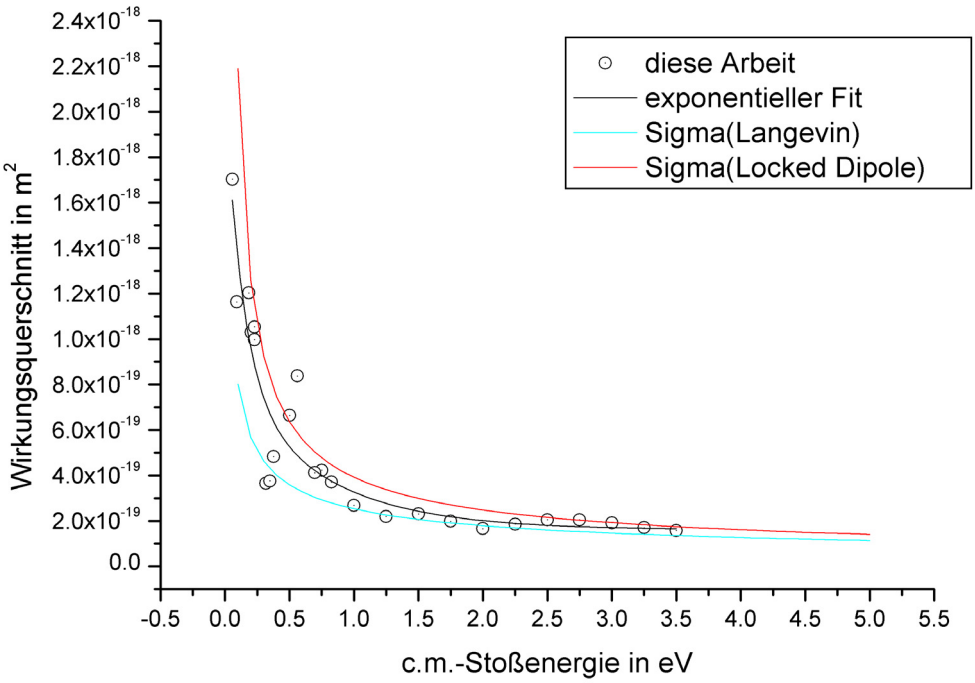

Abb. 6-1: comparison of Langevin and „Locked Dipole“ with experimental data

In conclusion, the goal of building a fully functioning vacuum machine to investigate ion-molecule reactions was reached in this study. The results of this study have identified experimental conditions and possible hindrances for this new machine and may altogether pave the way for future projects employing the same system.